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(58) Field of search
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(54) **Oxychlorination catalysts**

(57) Oxychlorination of ethylene to give vinyl chloride in a single step in the presence of a supported catalyst containing compounds of palladium, copper, iron, alkali metal and, optionally, rare earth metals.

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SPECIFICATION

Process for the manufacture of monohalogenated olefines and catalysts for use in such process.

This invention relates to the manufacture of monohalogenated olefinic compounds by the oxyhalogenation of the corresponding olefines. The invention is also concerned with a catalyst composition useful in such a precess.

Processes for the manufacture of monohalogenated olefines by the oxyhalogenation of the corresponding olefine have been beset with difficulties. This is particularly true with the oxychlorination of mono-olefines especially of ethylene. There is every incentive to provide an efficient process for the oxychlorination of ethylene in a single stage to give vinyl chloride as the major product. Indeed very many attempts have been made with much expenditure of time and money to provide such a process. Such attempts in the main have been directed at providing an effective catalyst for the oxychlorination process. Many combinations of catalysts and co-catalyst have been proposed. For example catalysts have been proposed comprising a compound of palladium and copper. However processes based on the use of known catalysts do have severe disadvantages. Thus in the oxychlorination of ethylene the disadvantages include poor conversions based on starting material, especially based on a chlorinating agent, poor selectivities to the desired vinyl chloride product, production of considerable amounts of undesired by-products or considerable burning of ethylene to give carbon oxides.

It is an object of the present invention to provide a novel, much improved oxyhalogenation process wherein said disadvantages are very much reduced and as such the process provides a most valuable constribution to the art.

According to one aspect of the invention we provide a process for the oxyhalogenation of a feedstock comprising an olefine to give a monohalogenated olefine which comprises bringing into reaction at elevated temperature in the gas phase an olefine with a source of halogen and molecular oxygen in the presence of a supported catalyst composition comprising a compound of palladium, a compound of copper, a compound of iron and a compound of an alkali metal.

It is preferred to include in the catalyst composition a compound of a rear earth metal. Compounds of different rare earth metals may be employed. One suitable compound of a rare earth metal contains a significant amount of a compound of cerium.

As illustrative of the compounds of the alkali metals compounds of sodium and lithium may be mentioned. A compound of sodium is preferred.

The compounds of the metals incorporated in the catalyst composition are suitably but not necessarily the halides corresponding to the halogen of the monohalogenated compound which is produced. In an oxychlorination process, for example of ethylene the compounds of the metals are suitably the chlorides. In use in the oxychlorination process the composition may exist as a mixture of chlorides, oxychlorides, oxides and hydroxides. Compounds of metals such as nitrates, oxides, carbonates, oxalates and acetates may also be employed which are converted to the chlorides or said mixtures containing chlorides under the oxychlorination conditions.

Each component of the present catalyst composition has an intricate relationship with one or more of the components of the catalyst composition. While theories can be propounded by way of explaining the relationship the practical result is that unless all of the components are present the improved results of the present process will not be achieved. When the rare earth compound is incorporated in the catalyst composition said compound also shares a relationship with one or more of the other components of the composition and in turn contributes a beneficial result in the efficiency of the process.

We find according to a further and most valuable feature of the invention that there is an intricate relationship between the atomic ratios of the various metals in the present catalyst composition. When using these atomic ratios and particularly when using the preferred atomic ratios the advantages of the present process become more apparent. These advantages include high conversions of the chlorinating agent, high selectivities, comparitively low formation rates of undesired products e.g. dichloroethylene and 1,1,2 - trichloroethane and comparitively low burning of ethylene. Such advantages have not been obtained in prior processes.

It is preferred to employ an atomic ratio of palladium to copper in the range 1 atom of palladium to 0.25 to 10 atoms of copper. Typical catalysts contain 1 atom of palladium per 1 to 3 atoms of copper and in particular 1.7 to 2.8 atoms of copper.

The atomic ratio of iron to palladium is suitably in the range 1:1 to 20:1. Preferably this atomic ratio is in the range 4 to 10 atoms of iron per atom of palladium.

The atomic ratio of rare earth metal to palladium is suitably in the range 1.1 to 15.1. Preferably this atomic ratio is in the range 3:1 to 8:1.

The atomic ratio of alkali metal to palladium is suitably in the range 10:1 to 30:1. Preferably this atomic ratio is in the range 15:1 to 25:1.

The proportion by weight of palladium based on the supported catalyst is preferably in the range 0.05% to 0.5%.

The catalyst may be supported on known carriers such as for example silica and alumina. The surface area of the support can be varied widely but is usually in the range 0.1 to 20 m^2/g.

The supported catalyst may be employed in fixed, moving or fluidised beds and of appropriate particle size.

The feed stock employed in the present invention is essentially olefinic. Olefine reactants which can be employed include for example, ethylene, propylene, straight and branched-chain olefines containing four or more carbon atoms and cyclic olefine such as cyclohexene.

A particularly suitable olefine for use in the present invention is ethylene. The olefine may also contain a saturated hydrocarbon component, for example, commercially available feedstocks consisting

essentially of ethylene but also containing a small proportion of ethane.

The reaction temperatures employed are dependent to a considerable extent on the reactant employed. With ethylene suitable reaction temperatures are in the range 250°C to 400°C, preferably 300°C to 370°C.

The source of chlorinating agent in the present process may be chlorine, hydrogen chloride or substances such as ammonium chloride which on heating decompose to give hydrogen chloride. More suitably the source of the chlorinating agent is hydrogen chloride.

The source of oxygen may be oxygen itself, air or oxygen enriched air. When using oxygen itself the organic product, by-products and water are removed and the residual exit gases after suitable monitoring and analysing can be returned to the system.

The molar ratios of ethylene, oxygen and hydrogen chloride are preferably such as to provide 0.5 to 1 mole of oxygen and 0.9 to 1.5 moles hydrogen chloride for each mole of ethylene. Most suitably the relative proportion of ethylene: hydrogen chloride is approximately 1:1.

In the present process the desired products can be recovered by conventional means. Any dichloroethanes in the crude organic product can be recycled thereby giving more of a desired vinyl chloride product.

The present invention also includes a supported oxychlorination catalyst composition as hereinbefore described.

The following Examples illustrate the invention.

EXAMPLE 1

The support for the catalyst was an alpha-alumina of surface area 0.6 m^2/g and of particle size in the range 50 to 100 μm. To a weak solution of hydrochloric acid were added 0.5g Pd Cl_2, 0.48g Cu $Cl_2 2H_2O$, 3.65g Fe Cl_3, 6.3g Ce $Cl_3.7H_2O$ and 3.95g NaCl. 120g of the support were added to the solution containing the metal chlorides. The mixture was stirred continuously at 100°C to 150°C for a period of ½ hour to 1 hour by which time the catalyst (CatalystA) was dry.

Other catalysts were prepared in a similar manner and are disclosed in Table I.

TABLE I

	Atomic Ratios of Metals				
Catalyst	*Pd*	*Cu*	*Fe*	*Ce*	*Na*
A	1	1	8	6	24
B	1	2	5	6	19
C	1	3	3	5	16
D	1	2	4	5	17
E	1	2	5	8	21
F	1	2	16	0	24

EXAMPLE 2

The apparatus comprised a vertical, heat-resistant glass tube 30cm long and 2.5cm diameter surmounted by an electric furnace. The tube contained 95g of the catalyst(s). Ethylene, hydrogen chloride and air were passed separately into the tube and maintained the catalyst in fluidised bed conditions and product was recovered and analysed by conventional means. The ratio (air calculated as oxygen) of C_2H_4:HCl:O_2 was 1:1:0.87.

The temperature conditions and results were as shown in Table II.

TABLE II

Temp °C	*Catalyst*	*% conversion of HCl*	*Selectivity % v/v to specific products*			*Burning*
			VC	*1,1-di*	*EDC*	*CO_2*
364	A	91.5	47.8	9.6	32.2	8.7
362	B	91.6	57.5	4.6	29.0	7.1
365	C	90.6	40.9	8.5	36.5	14
365	D	86.4	44.0	7.5	36.7	12.2
361	E	83.2	56.9	9.0	22.0	12.1
362	F	84.2	51.7	9.0	27.1	12.2

CONVERSION

By way of comparison three catalyst G, H and I were prepared in the broad manner described in Example 1 but which did not contain all the necessary components of the catalysts according to the invention. They were as disclosed in Table III.

TABLE III

	Atomic Ratios of Metals				
Catalyst	*Pd*	*Cu*	*Fe*	*Ce*	*Na*
G	1	0	16	0	24
H	1	2	0	5	17
I	1	0	10	6	24

Runs were carried as described in Example 2 and the results are shown in Table IV.

TABLE IV

Temp	*Catalyst*	*% conversion of HCl*	*Selectivity % v/v to specific products*			
			VC	*1,1-di*	*EDC*	*Burning CO_2*
362°C	G	34.6	54.1	1.76	14.7	29.5
367°C	H	78.9	34.2	12.5	38.2	14.6
361°C	I	44.7	60.5	3.6	11.9	23.7

In the above Examples,
VC means Vinyl Chloride
1,1-di means 1,1-dichloroethane
EDC means 1,2-dichloroethane

CLAIMS

1. A process for the oxyhalogenation of a feedstock comprising an olefine to give a monohalogenated olefine which comprises bringing into reaction at elevated temperature in the gas phase an olefine with a source of halogen and molecular oxygen in the presence of a supported catalyst composition comprising a compound of palladium, a compound of copper, a compound of iron and a compound of an alkali metal.

2. A process as claimed in Claim 1 wherein a compound of a rare earth metal is also incorporated in the catalyst composition.

3. A process as claimed in Claim 1 or Claim 2 in which a compound of sodium is employed as the alkali metal compound.

4. A process as claimed in any one of the preceding claims in which the atomic ratio copper to palladium in the catalyst composition is in the range 0.25:1 to 10:1.

5. A process as claimed in Claim 4 in which the atomic ratio of copper to palladium in the catalyst composition is 1:1 to 3:1.

6. A process as claimed in Claim 5 in which the atomic ratio of copper to palladium in the catalyst composition is in the range 1.7:1 to 2.8:1.

7. A process as claimed in any one of the preceding claims in which the atomic ratio of iron to palladium in the catalyst composition is in the range 1:1 to 20:1.

8. A process as claimed in Claim 7 in which the atomic ratio of iron to palladium in the catalyst composition is in the range 4:1 to 10:1.

9. A process as claimed in any one of the preceding claims in which the atomic ratio of rare earth metal to palladium in the catalyst composition is in the range 1:1 to 15:1.

10. A process as claimed in any one of the preceding claims in which the atomic ratio of rare earth metal to palladium in the catalyst composition is in the range 3:1 to 8:1.

11. A process as claimed in any one of the preceding claims in which the atomic ratio of alkali metal to palladium in the catalyst composition is in the range 10:1 to 30:1.

12. A process as claimed in claim 9 in which the atomic ratio of alkali metal to palladium in the catalyst is in the range 15:1 to 25:1.

13. A process as claimed in any one of the preceding claims in which the proportion by weight of palladium in the supported catalyst composition is in the range 0.05% to 5% by weight.

14. A process as claimed in any one of the preceding claims in which the compounds of the metals in the catalyst composition are the halides corresponding to the halogen of the monohalogenated compound which is produced.

15. A process as claimed in Claim 14 in which the halides of the metals are chlorides.

16. A process as claimed in Claim 15 in which the source of the halogen reactant is hydrogen chloride.

17. A process as claimed in Claim 15 or Claim 16 in which the olefine ractant is ethylene.

18. A process according to Claim 17 which is carried out at a reaction temperature in the range 250°C to 400°C.

19. A process according to Claim 18 which is carried out at a reaction temperature in the range 330°C to 370°C.

20. A process as claimed in any one of the preceding Claims 15 to 19 in which the molar ratios of ethylene, oxygen and hydrogen chloride are such as to provide 0.5 to 1 mole of oxygen and 0.9 to 1.5 moles hydrogen chloride for each mole of ethylene.

21. A process as claimed in Claim 1 substantially as described with reference to Example 2.

22. Monohalogenated olefines whenever produced by a method according to any one of the preceding claims.

23. A supported, oxyhalogenation, catalyst composition comprising a compound of palladium, a compound of copper, a compound of iron, and a compound of an alkali metal as described in any one of the preceding Claims 1 to 15.

24. A supported, oxyhalogenation catalyst composition substantially as described in Example 1.

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